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**Real-time monitoring of nutrients and dissolved organic matter in rivers: capturing event dynamics, technological opportunities and future directions**

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## Abstract

Excessive riverine nutrient concentrations threaten aquatic ecosystem structure and functioning and can pose substantial risks to human health. Robust monitoring strategies are therefore required to generate reliable estimates of river nutrient loads and to improve understanding of the catchment processes that drive nutrient fluxes. Furthermore, these data are vital for prediction of future trends under changing environmental conditions and thus the development of appropriate mitigation measures. In recent years, technological developments have led to an increase in the use of *in-situ* nutrient analysers, which enable measurements at far higher temporal resolutions than can be achieved with discrete sampling and subsequent laboratory analysis. In this paper, we review the principles underlying the key techniques used for *in-situ* nutrient monitoring and highlight both the advantages, opportunities and challenges associated with high-resolution sampling programs. We then suggest how adaptive monitoring strategies, comprising several different temporal sample frequencies, controlled by one or more 'trigger variables' (e.g. river stage, turbidity, or nutrient concentration), can advance our understanding of catchment nutrient dynamics while simultaneously overcoming many of the practical and economic challenges encountered in typical *in-situ* river nutrient monitoring applications. We present examples of short-term variability in river nutrient dynamics, driven by complex catchment behaviour, which support our case for the development of monitoring systems that can adapt in real-time to rapid changes in environmental conditions. Finally, we suggest future research directions based on emerging technologies in this field.

## 1. Introduction

Rivers transport and transform nutrients between terrestrial, aquatic, marine and atmospheric systems, thereby playing a key role in global biogeochemical cycling (Ensign and Doyle, 2006; Battin *et al.*, 2008; Hood *et al.*, 2015). Any increase in river nutrient concentrations, whether as a consequence of farming practices or urbanisation, may have substantial implications for aquatic ecosystem structure and functioning (Smith and Schindler, 2009). Eutrophication can result in algal blooms that decrease dissolved oxygen levels, change pH balances, and increase water turbidity. Such changes will impact river habitat and biodiversity, particularly the abundance of sensitive aquatic species (Camargo *et al.*, 2005; Friberg *et al.*, 2010). High river nutrient concentrations may also affect human health and well-being by threatening aquatic ecosystem services, such as freshwater provision for drinking and irrigation, maintenance of fisheries for food, recreational opportunities and aesthetic qualities such as taste, colour or odour (MEA, 2005; Bennett *et al.*, 2009). Nitrate concentrations  $> 50 \text{ mg L}^{-1}$  in drinking water can cause methemoglobinemia in humans, particularly infants, and may be associated with other adverse health effects including cancer and diabetes (Ward *et al.*, 2005). Consequently, drinking-water treatment plants incur higher costs to reduce excessive nutrient levels to within quality standards, with some organic carbon fractions reacting to form potentially mutagenic and carcinogenic disinfectant by-products during the treatment process (Carpenter *et al.*, 2013).

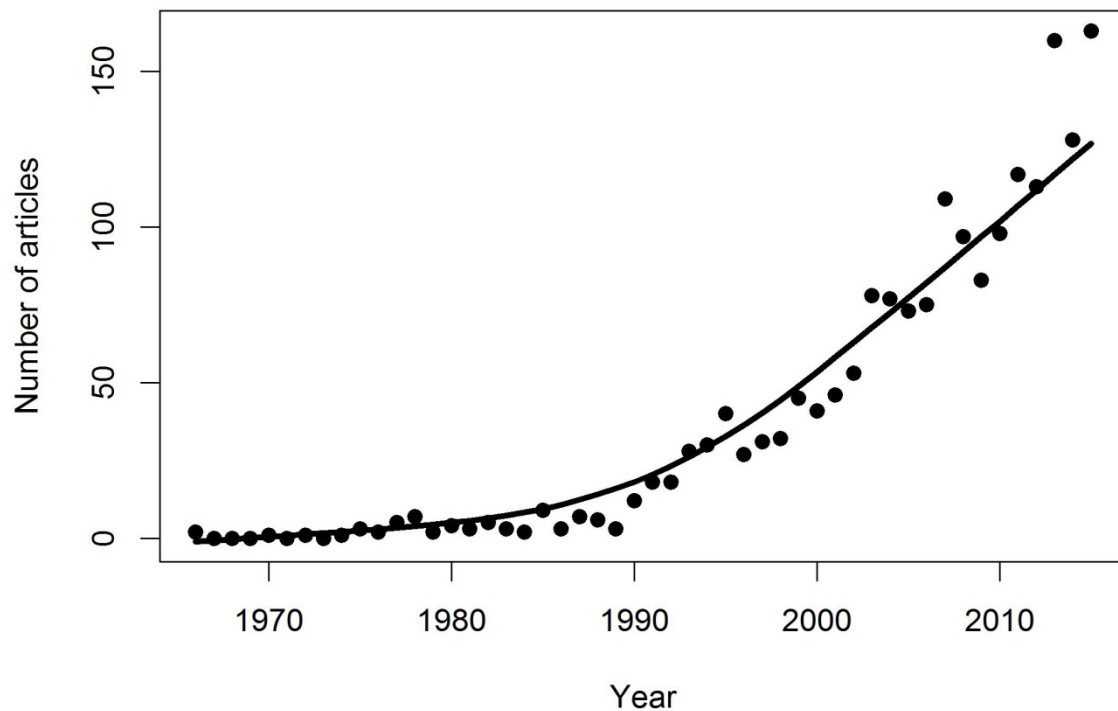
The environmental impacts of excessive nutrient concentrations highlight the need to understand spatial and temporal variability in river nutrient dynamics. Effective nutrient monitoring strategies can support catchment management by detecting the impact of natural phenomena (e.g. drought) or anthropogenic activities (e.g. land-management practices or point discharges) on river water quality. The resulting information may also help in determining ecological flows and detecting suitable locations or times for water abstraction (Bartram and Rees, 1999; Palmer and Bernhardt, 2006). Long-term continuous datasets of river nutrient concentrations enable the assessment of patterns, trends, and shifts in system behaviour (Burt *et al.*, 2010) and also improve our understanding of the relationships with catchment processes that drive such variability (Bowes *et al.*, 2009). For example, nitrate concentrations measured in both UK and US rivers since the 1930s exhibit marked increases through the post-war period and coincide with increasing applications of inorganic nitrogen fertiliser to arable farmland (McIsaac and Libra, 2003; Burt *et al.*, 2010). More recently, monitoring data have been used to investigate links between river nutrient fluxes and upstream watershed management, demonstrating the potential for land management practices to both elevate and alleviate river nutrient loading (Valiela and Bowen, 2002; Lassaletta *et al.*, 2009). This information helps any assessment of the effectiveness of mitigation measures to counteract nutrient loading and support future decisions relating to land and river management (Bowes *et al.*, 2009), particularly in the context of predicted future changes in climate that are expected to drive shifts in river nutrient loads (Whitehead *et al.*, 2009). The importance of this is reflected in national legislation and multilateral agreements (e.g. European Union Water Framework Directive or WFD, 2000/60/EC) relating to monitoring, and in some cases also improving, the status of freshwater environments.

River nutrient monitoring has evolved over time from sporadic, ad-hoc, sampling of local rivers (e.g. Casey and Clark, 1979) to the establishment of national river water quality data systems with standardised sampling protocols, such as the UK Harmonised Monitoring Scheme that commenced

in the mid-1970s (Simpson, 1980) and the General Quality Assessment Scheme that operated from 1990 to 2009 (Environment Agency, 2016) to the implementation of multi-lateral agreements that standardise water quality assessment procedures across member states and, in some cases, across multi-national drainage basins (e.g. European Union WFD; Hering *et al.*, 2010). Traditionally, the frequency and coverage of river water sampling has been constrained by practical issues related to the costs of field personnel and laboratory analysis. Autosamplers enable short-term increases in sampling frequency but have limited volumes and samples may degrade if not preserved or processed quickly (Bende-Michl and Hairsine, 2010). Consequently, the spatial and temporal resolutions of many river nutrient monitoring systems and observational networks have been relatively low, despite a growing body of evidence demonstrating that nutrient concentrations in lotic environments can exhibit highly dynamic and non-linear behaviour in both time and space (Wade *et al.*, 2012; Halliday *et al.*, 2014; Bieroza and Heathwaite, 2015; Krause *et al.*, 2015). Complex nutrient dynamics can arise from variability in climate forcing or changes in environmental management practice as well as accumulation and release of material and associated first flush effects (Krause *et al.*, 2015). For example, increased flows driven by storm events can mobilise sediments and account for a large proportion of the annual total phosphorus export from river catchments (Bowes *et al.*, 2009), while Pellerin *et al.* (2011) observed high diurnal and event-based variability in the flux of nitrate and dissolved organic matter (DOM) associated with the flushing of shallow hillslope flow paths during spring snowmelt. Such results indicate that river nutrient concentrations are commonly discharge-driven to a large extent, yet often the variability in river hydrological regimes is inadequately captured by the regular frequency of standard water quality sampling programmes. Consequences of inadequate sampling frequencies include missing key pulses of nutrients during short-term events, and potentially underestimating long-term nutrient fluxes by up to an order-of-magnitude (Mellander *et al.*, 2012; Neal *et al.*, 2012; Krause *et al.*, 2014).

In recent years, developments in sensing technologies, coupled with decreasing costs, have led to increased usage of *in-situ* analysers to monitor key macronutrient (i.e. C, N, P) concentrations, species (e.g. NO<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub>) and composition (e.g. DOM; spectral slope and fluorescence spectra) (Figure 1). This technology enables monitoring at far higher frequencies than can be achieved with discrete sampling and subsequent laboratory analysis and, importantly, allows the pairing of nutrient and river flow measurements at the same temporal resolution. Data generated from *in-situ* high-resolution (i.e. frequencies of 10<sup>-1</sup> to 10<sup>-3</sup> h) monitoring (HRM) can yield valuable new insights into the drivers, controls and organisational principles of nutrient dynamics in lotic ecosystems (Bowes *et al.*, 2009), and may help to identify future responses to environmental pressures and potential tipping points in system behaviour (Wade *et al.*, 2012). In addition to characterising nutrient fluxes at catchment outlets, deconvolution of HRM data may also enhance our capacity to discover more about the time-variant activation of catchment source area dynamics (Krause *et al.*, 2014). HRM also has potential applications in improving legislative monitoring strategies (Halliday *et al.*, 2015), enhancing water body classification schemes (Skeffington *et al.*, 2015) and providing an early warning of potential harmful by-products or bacteria (Bridgeman *et al.*, 2015; Li *et al.*, 2016). However, HRM equipment can be costly to run and difficult to maintain, and HRM is not necessarily appropriate for all river nutrient monitoring applications. This paper aims to outline the principles of measurement and the major advantages and disadvantages associated with contemporary *in-situ* nutrient sensing technologies, and demonstrate the potential for real-time adaptive monitoring to provide new insights into processes operating within river catchments whilst overcoming some of

the challenges associated with the collection and analysis of data generated through HRM. We use case studies to demonstrate the applicability of this approach to a diversity of environments. Finally, we conclude by highlighting key areas for future research where *in-situ* monitoring data may improve understanding of nutrient dynamics and ecosystem processes within river catchments.



**Figure 1:** Number of articles published by year listed on Web of Science matching the following search terms: (high-resolution OR continuous OR automated) AND (nutrient OR NO<sub>3</sub>\* OR nitrate OR nitrogen OR ammonia OR ammonium OR NH<sub>3</sub>\* OR NH<sub>4</sub>\* OR doc OR \*dom OR tryptophan OR PO<sub>4</sub>\* OR phosphate OR phosphorus) AND (sampling OR monitoring OR sensor OR analy\*) AND (stream OR river). Data from 2016 are excluded to avoid potential issues with as-yet-uncatalogued articles.

## 2. Principles of *in-situ* nutrient monitoring techniques

*In-situ* determinations of macronutrient concentrations, species and compositions utilise recent technological advances in electrochemical detection, colorimetry and optical methods using absorbance or fluorescence, which offer increasing opportunities for HRM. Table 1 summarises the parameters which are generally measured via each technique, along with the measurement ranges and the associated accuracy

<Table 1: Summary of commonly-used measurements methods for *in-situ* nutrient monitoring and the associated accuracy, range and maintenance requirements for each method>

### 2.1 Electrochemical detection

The use of electrochemical detection for nutrient determination using Ion-Selective Electrodes (ISEs) is well established and the technology has been miniaturised to enable *in-situ* quantification of NO<sub>3</sub>, NH<sub>3</sub> and pH (Le Goff *et al.*, 2002; Merks, 1975; Collings, 2003). ISEs use direct potentiometry between a sensing electrode and a reference electrode (Figure 2a) with measurement ranges typically spanning at least three orders of magnitude (YSI, 2016; Hach, 2016). Unlike many optical techniques (see below), ISEs are not influenced by water colour or turbidity, but are often subject to significant drift and ionic interferences (de Marco *et al.*, 2007) and can also suffer from systematic errors if the ionic activity of the calibration buffer solution is markedly different to that of the field sample (Le Goff *et al.*, 2002). However, newer sensors have been developed which are able to combat some of the biggest problems with ISEs. For example, Le Goff *et al.* (2002) describes a nitrate ISE that measures over a reduced concentration range but which remains stable for up to four months in the field, and Tang *et al.* (2012) present a solid-state ISE for analysis of NO<sub>3</sub>.

### 2.2 Colorimetry

Colorimetric methods have been developed to quantify NO<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub>, PO<sub>4</sub> and total phosphorus (TP) using either submersible microfluidic technology or bank-side analysers. Samples are mixed with reagents to generate coloured solutions which are then detected using photometry (Figure 2b). Colorimetric techniques generally have higher levels of precision and accuracy than ISEs, however their measurement range is reduced and usually spans one to two orders of magnitude (Patton and Kryskalla, 2011). Importantly, most colorimetric reactions are temperature-dependent and post-correction is required if water temperatures change significantly during deployment. In addition, sampling resolutions are constrained by the reaction time necessary for the colour change to completely develop, and turbid waters can influence measurements by altering the background water colour.

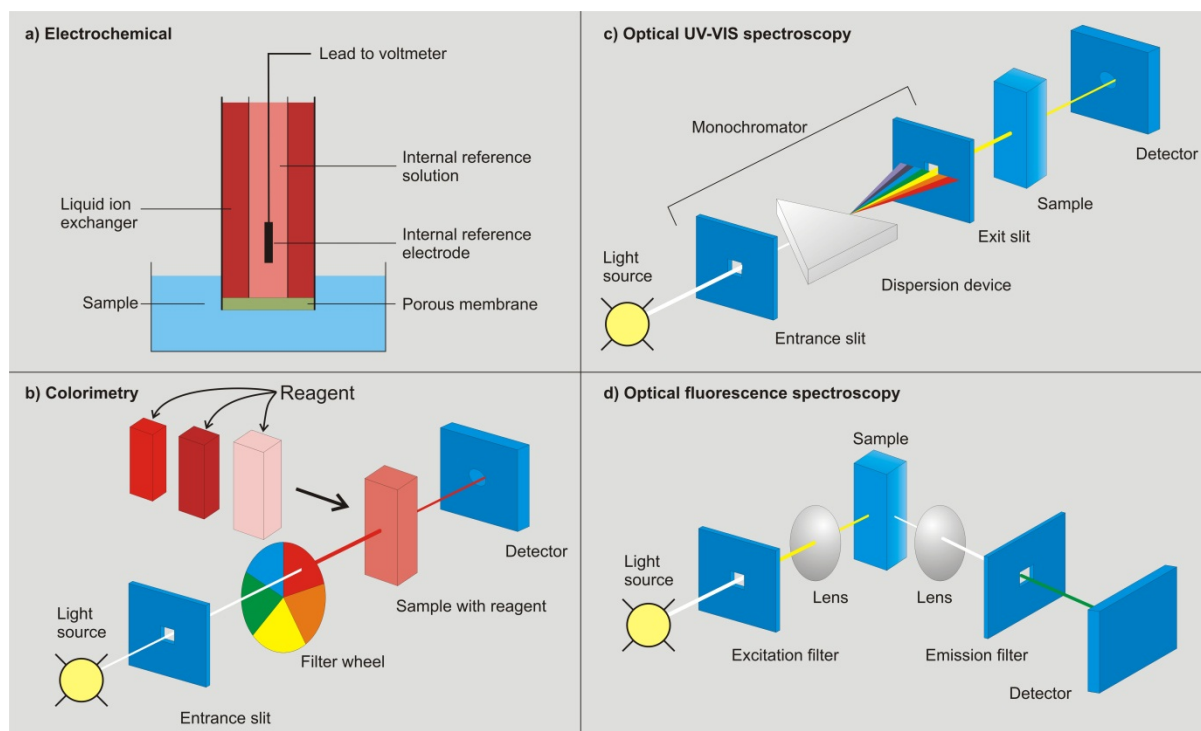
### 2.3 Optical UV-VIS spectroscopy

Optical sensors using ultraviolet spectroscopy provide a reagent-free method for determining a range of parameters including dissolved organic carbon (DOC) and NO<sub>3</sub>. The measurement principle is based on the spectral absorption of a sample at a defined wavelength (Figure 2c). Appropriate algorithms are necessary to convert the optical signal to concentration of the parameter of interest, and hence it is a proxy technique rather than a direct measurement of the parameter. The resulting data are usually of high resolution and highly precise and accurate, although this can vary depending upon the parameter required (van den Broeke *et al.*, 2006). Potential problems with optical interferences are similar to those associated with colorimetry when deployed in river water due to high sediment loads, debris and discolouration of the water. However, many commercially-available devices now incorporate algorithms to correct for interference by using secondary compensation wavelengths or, in some cases, the whole UV-VIS absorption spectrum.

#### 2.4 Optical fluorescence spectroscopy

Optical sensing using fluorescence has grown in popularity due to technological advances and reduced *in-situ* sensor costs. Single excitation-emission sensors quantify the light emitted from a sample at a particular wavelength when the sample is excited by a known wavelength of light (Figure 2d). While the *in-situ* sensors have a narrow wavelength range compared with their benchtop equivalents, they can target particular compound classes based on their fluorescent properties. Typically sensors are used to detect relatively low molecular weight compounds such as proteineous material and hydrocarbons, but can also be used to identify more complex macromolecular material which makes up the coloured DOM (CDOM) fraction. Specific wavelengths can be used to quantify parameters such as chlorophyll *a* and dissolved oxygen (DO). The measurements are rapid and have the potential to yield sub-five minute resolution data. The use of fluorescence has similar issues to UV optical sensors and is subject to interferences from turbidity (Saraceno *et al.*, 2009), bubbles, temperature (Watras *et al.*, 2011), shading and fouling. It is also important to determine absorbance at the relevant wavelengths to enable data post-processing as inner-filter effects caused by attenuation of excitation light and reabsorption of emitted photons (Downing *et al.*, 2012; Khamis *et al.*, 2015; Lakowicz, 2013).





**Figure 2:** Diagrammatic representation of principles of *in-situ* nutrient monitoring techniques for a) electrochemical, b) colorimetry, c) optical UV-VIS spectroscopy, and d) optical fluorescence spectroscopy.

## 2.5 Practical considerations

HRM is a powerful tool for hydrological and water quality research, although maintenance frequency is proportional to the sampling frequency and hence HRM may require more frequent maintenance compared with lower resolution sampling campaigns. To ensure the highest quality data from HRM systems, several issues must be considered to determine the most appropriate sensor type and monitoring location.

Firstly, power demand varies between sensor types, dataloggers and telemetry systems. Power is usually provided through batteries, fuel cells or solar panels, although for some bankside analysers mains power is the most suitable option given the higher power requirements associated with pumping water to the analyser. For batteries or fuel cells, regular checks are necessary to minimise instrument drop-outs and changes may be required once or more each month, particularly during winter when batteries become less efficient at lower operating temperatures. Solar panels provide a more sustainable alternative, although suitable siting is important as shaded areas may yield insufficient power generation, especially in winter when solar altitudes are low. Second, virtually all *in-situ* sensors are subject to fouling. Most *in-situ* sensors are submerged in the water body and can be susceptible to accumulation of sediment, biofilms, or other debris around the sensor. Fouling can also affect bankside setups, particularly in the tubing which carries the sample to the sensor. Technologies to reduce the impact of biofouling on sensors are now commercially available,

including anti-fouling coatings, automatic wipers or compressed air which seek to prevent, or clear, accumulated particulates and biofilm growth (Kotamäki, 2009; Conmy *et al.*, 2014). However, regular manual cleaning is required for most monitoring systems and should be considered a mandatory component of HRM programs (Jones *et al.*, 2014). Third, most sensors are affected to a degree by other environmental factors such as pH, temperature, electrical conductivity and turbidity (e.g. Downing *et al.*, 2012; Khamis *et al.*, 2015). These environmental variables vary through time and, unless explicitly accounted for by the sensor, should be monitored alongside the parameter of interest so that post-processing corrections can be applied. Furthermore, although routine onsite calibrations can achieve increasingly accurate measurements (Saraceno *et al.*, 2009), sensor outputs should be ‘ground-truthed’ using samples that are independently measured under controlled conditions in the laboratory.

Careful consideration of these issues should minimise sensor down-time and ensure accurate and high-quality data output. Inevitably, however, sensors will be subject to occasional mechanical failure, particularly when deployed to monitor nutrient behaviour during storms where the risk of damage is increased. Therefore, sensor checking should be carried out routinely so that problems can be quickly identified and fixed. Telemetry systems are invaluable in this respect as sensor performance or power supply issues can be quickly identified (Glasgow *et al.*, 2004).

### **3. High resolution *in-situ* river nutrient monitoring**

#### ***3.1 Opportunities and challenges***

The use of *in-situ* sensing technologies to monitor nutrients and dissolved organic matter (DOM) in riverine environments has lagged behind other aquatic systems (Johnson *et al.*, 2007; Saraceno *et al.*, 2009). *In-situ* monitoring of absorbance and fluorescence to investigate the spatial and temporal dynamics of DOM, nitrate and primary production were first undertaken ~20 years ago in marine systems (Daniel *et al.*, 1995; Pegau *et al.*, 1995; Chen, 1999). This early work typically involved relatively large instruments with high power consumption, and their deployment was largely restricted to research vessels (e.g. Daniel *et al.*, 1995). Much of this instrumentation was engineered to withstand high pressures to enable deep sea deployment (e.g. Finch *et al.*, 1998) and the increased cost limited applications of this technology to marine systems. However, recent advances and decreased costs have facilitated the use of HRM equipment in freshwater systems to improve understanding of nutrient and DOM dynamics for a range of freshwater ecosystems, including urban (Wade *et al.*, 2012; Halliday *et al.*, 2015), agricultural (Bieroza *et al.*, 2014; Outram *et al.*, 2014) and alpine rivers (Pellerin *et al.*, 2011). Advances in field deployable monitoring technologies are enhancing our ability to understand the linkages between climate, catchment properties, and hydrological/ biogeochemical fluxes (Krause *et al.*, 2015) and to detect environmental change at finer spatial and temporal scales (Sobczak and Raymond, 2015). This section will outline the capacity and limitations of HRM in the context of improving hydro-ecological understanding of lotic systems and associated interfaces.

The 'traditional' approach for monitoring nutrient and pollutant loads has involved the collection of discrete spot samples, either manually or via autosamplers, to estimate fluxes and annual loads (e.g. Johnes, 2007). However, while monthly or fortnightly sampling regimes may be sufficient to characterize lentic systems (Pobel *et al.*, 2011), they are unable to adequately represent the dynamic behaviour of lotic system potentially contributing to serious errors in load estimation (Johnes, 2007; Cassidy and Jordan, 2011; Lloyd *et al.*, 2016). For example, while weekly spot sampling may be sufficient to detect inter-annual variability in N and P loads, significant information on the flow extremes (i.e. shape of the frequency distribution) may be lost when compared to sub-hourly monitoring (Bieroza *et al.*, 2014). Other studies highlight the need to consider catchment behaviour (i.e. flashy vs muted flow response to storm events) when determining monitoring frequency; for example, Cassidy and Jordan (2011) suggested that for a flashy catchment sub-hourly (i.e. 20 mins) HRM is required to accurately quantify the P load as even storm event triggered sampling led to high uncertainty. However, Lloyd *et al.* (2016) highlighted the need for a systemic approach to handling errors associated with HRM flux estimates (N and P) as, in many cases, sampling at high resolution results in tradeoffs between measurement precision and accuracy.

Significant pulses of nutrients and DOM can be rapidly mobilized and transported through the river network during storm events (Hinton *et al.*, 1997). Recently, *in-situ* HRM using field deployable UV-absorbance sensors has provided new insight into C dynamics during storm events (e.g. Jeong *et al.*, 2012; Strohmeier *et al.*, 2013; Table 2). Rainfall intensity has been identified as a key control on the form of C transported (i.e. dissolved vs particulate) and HRM has enabled C sources and flow paths to be traced (Jeong *et al.*, 2012) thus improving our understanding of how these systems are likely to respond to climatic change. Furthermore, recent sub-hourly monitoring of N & P in the UK has highlighted important links between meteorological conditions (event and antecedent conditions) and in-channel nutrient fluxes (Outram *et al.*, 2014; Table 2). Such information is needed when developing adaptation strategies for nutrient enriched catchments, particularly given anticipated changes in the magnitude and frequency of extreme meteorological and hydrological events (Kendon *et al.*, 2014).

In addition to event-based nutrient dynamics, HRM can also offer new insights into hydro-ecological processes at temporal scales ranging from diurnal to seasonal. For example, *in-situ* fluorometers have enabled identification of distinct diurnal dynamics of organic C in rivers (Spencer *et al.*, 2007; Worrall *et al.*, 2015; Table 2) and lakes (Watras *et al.*, 2015). Biological activity was suggested as the primary driver of these patterns (Spencer *et al.*, 2007; Watras *et al.*, 2015); however, Spencer *et al.*, (2007) suggest that photolysis may also be an important mechanism. Moreover, Worrall *et al.*, (2015) focused on the links between abiotic factors and diurnal DOC cycles for the River Dee, UK. Using continuous UV absorbance data they suggested residence time and the accumulated temperature of water parcels (linked to day length) were the main drivers of diurnal patterns. *In-situ* FDOM monitoring (ex. 365 nm; em. 470 nm) coupled with discrete sampling and laboratory analysis revealed distinct seasonal changes in DOM composition (i.e. higher aromatic/molecular weight during the freshet period) for a river draining a mountainous river basin (Voss *et al.*, 2015). Wilson *et al.* (2013) also employed *in-situ* FDOM sensors to reveal seasonal changes in event based DOC fluxes. Distinct peaks in DOC quantity and bio-availability were associated with summer storm events highlighting the utility and advantage of *in-situ* HRM for tracking long term changes in DOC flux.

Large scale monitoring projects/schemes for legislative purposes (e.g. for the WFD) were devised based on data obtained through discrete sampling and subsequent laboratory analysis. Through the increased availability of HRM data it is becoming increasingly apparent that the limited sensitivity of traditional sampling methods leads to significant errors in WFD chemical class assignment, constraining our ability to detect trends (Skeffington *et al.*, 2015). For example, HRM of NO<sub>3</sub> and TP on the River Wylfe (Wiltshire, UK) showed that annual loads can be significantly underestimated if only daily sampling regimes are used (Lloyd *et al.*, 2016). High frequency monitoring of an urban stream in southern England identified distinct diurnal (in stream production) and seasonal (growing season) variability in parameters used to classify WFD chemical status (e.g. temperature, dissolved oxygen and P). This highlights the need to specify specific windows for WFD sampling as spot sampling in dynamic river systems can lead to spurious inferences regarding WFD status (Halliday *et al.*, 2015). Bowes *et al.* (2012) used high resolution P records to differentiate between sewage treatment works (STW) and diffuse and in-channel sources to confirm the STW was operating within consent limits. This research suggests that in addition to increasing the resolution of routine legislative monitoring in some cases, the way that WFD limit criteria are designed should also be reviewed where and when necessary. For example, WFD limits for soluble reactive phosphorus (SRP) are currently based around mean annual concentrations (UKTAG, 2013), the calculation of which is highly impacted by the sampling strategy. Therefore, there is an argument for developing more intelligent and robust limit guidelines for classifying water quality status. Furthermore, there is still a lack of a WFD classification in the UK for NO<sub>3</sub> and at present the Drinking Water Directive (98/83/EC) acts as a guideline for river water NO<sub>3</sub> concentrations but does not explicitly define limits required to meet good status.

There is increasing evidence that HRM data will improve our understanding of catchment nutrient dynamics particularly during 'active' periods. For example, simple hysteresis indices have been revised to improve understanding of nutrient transport processes in agricultural catchments (Bieroza and Heathwaite, 2015; Lloyd *et al.*, 2016). In addition, contemporary sensors provide the means to identify and monitor DOM processing *in-situ*, particularly as advances in LED technology mean monitoring using a suite of *in-situ* optical techniques (i.e. fluorescence and absorbance at different wavelengths) is becoming economically viable. The more detailed optical map provided can offer new insight into DOM dynamics in riverine environments enabling us to monitor both DOM quality and quantity continuously (Spencer *et al.*, 2007). Yet there are still significant challenges in achieving accurate *in-situ* measurement of DOM and other nutrients and these new UV-sensors should be seen as complementing, not replacing, traditional grab sampling (Sobczak and Raymond, 2015). There is a particular need to compensate for temperature and turbidity interference (Downing *et al.*, 2012; Khamis *et al.*, 2015) and account for seasonal variability in background water composition (Wilson *et al.*, 2013). Subsequent analysis of these high resolution data also requires careful consideration as the assumptions of many statistical tests are violated for time series data due to temporal auto-correlation and heteroscedasticity (Lloyd *et al.*, 2014). Furthermore, the maintenance and calibration schedules need to be carefully considered to ensure data quality as, even in pristine systems, fouling can lead to sensor drift over relatively short time intervals (Jones *et al.*, 2014). However, in some cases *in-situ* analysis can yield more accurate measurements than those produced by more traditional analytical methods. For example, Bieroza and Heathwaite (2016) demonstrated that measurement errors arising from short-term chemical changes in grab samples (i.e. those that

occur between sample acquisition and laboratory analysis) masked diurnal patterns in P and OM that were otherwise detected by *in-situ* analysers.

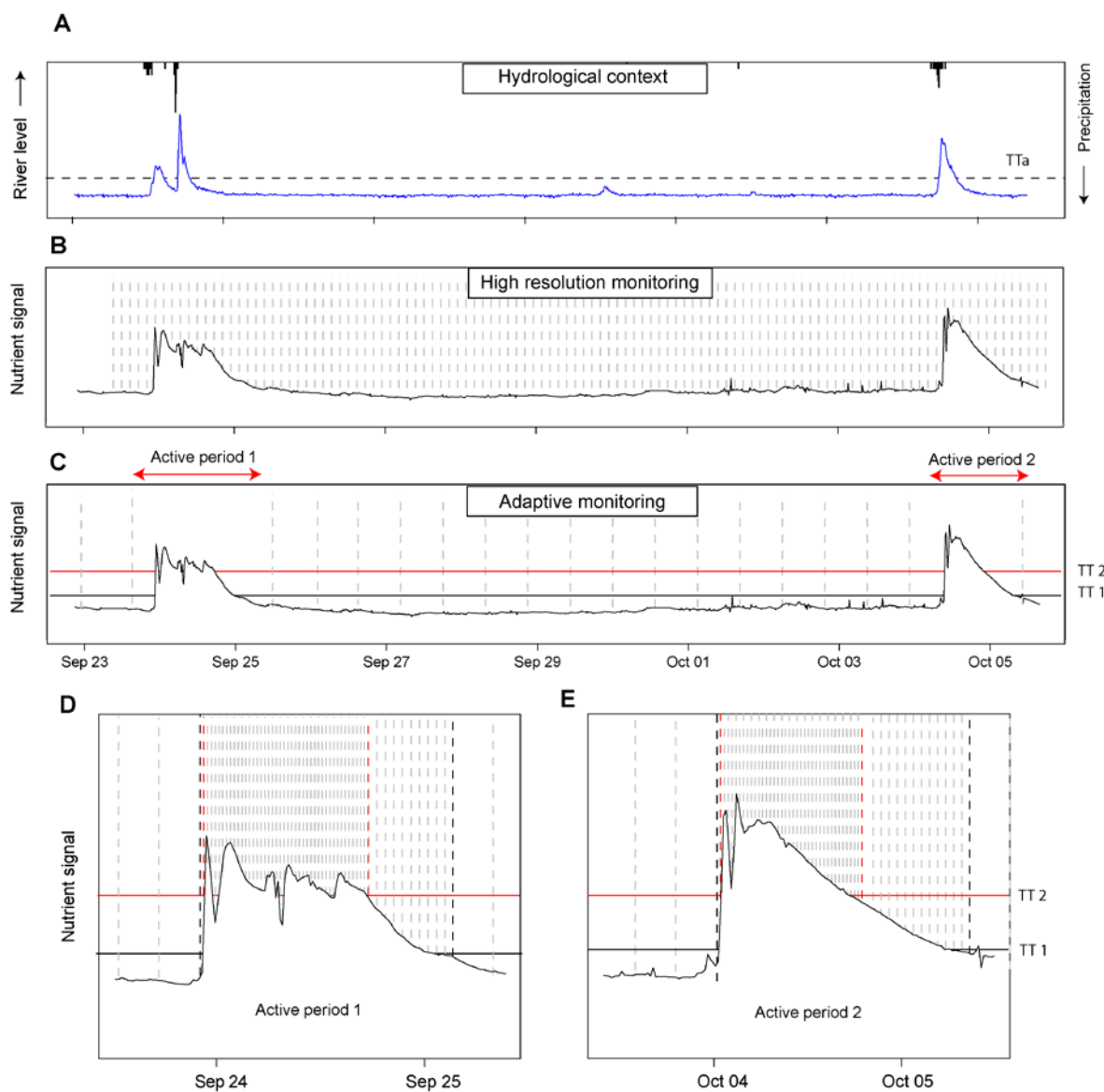
**<Table 2:** Summary of published studies on *in-situ* nutrient monitoring highlighting study duration, nutrients investigated, analysis methods employed and time required for processing>

### 3.2 Adaptive monitoring: a way forward?

While current studies using HRM are providing new insights into nutrient/DOM dynamics at a range of spatiotemporal scales, monitoring resolution is often limited by power consumption and data storage capacity (Downing *et al.*, 2009). Given the pulsed behaviour exhibited by many aquatic ecosystems (Junk *et al.*, 1989; Tockner *et al.*, 2000) conventional modern HRM schemes operating at hourly or sub-hourly resolution can result in significant data redundancy. For example extended periods of low biogeochemical activity or variability often occur during low flow periods (see Figures 3a and 3b). The unnecessarily high resolution of sampling can result in excessive memory and power consumption, and for certain monitoring techniques can increase maintenance requirements and waste generation (i.e. P analysers; Table 2). Conversely, during biogeochemically ‘active’ periods (e.g. high flow events) the resolution of many conventional HRM schemes is too coarse for detailed event characterization (Figure 3b). Thus, for monitoring dynamic riverine systems or examining eco-hydrological processes that exhibit strong non-linear properties, an adaptive monitoring approach is required (cf. Krause *et al.*, 2015). Here differing monitoring frequencies can be triggered based on the variable of interest (e.g. N or P), a surrogate/driver variable (e.g. level, electrical conductivity, turbidity, rainfall) or combination of variables. For example two thresholds (TT1 & TT2) can be defined based on the concentration of a nutrient of interest (Figure 3c, 3d, 3e). Using these thresholds as triggers to alter the monitoring frequency enables the capture of (i) the first flush and peak flow at very high resolution, and (ii) the recession at moderate resolution. If necessary, an additional threshold (TTa), such as river level, can be included to avoid triggering a change in monitoring frequency due to anomalous sensor readings. In this scenario the nutrient concentration (TT1) and river stage (TTa) must both be exceeded to initiate a change in monitoring frequency (Figure 3a and 3c). Furthermore, to avoid a ‘yo-yo’ effect, where the monitoring state alternates rapidly between two frequencies, additional logic commands can be included (e.g. switch from state TT2 to TT1 only when the previous three readings fall below a defined threshold). Finally, as telemetry has become more versatile and reliable, monitoring frequencies can reliably be changed remotely and in real-time, and warning alarms can also be triggered if defined thresholds are breached (Othman and Shazali, 2012).

The science questions to be addressed are particularly important when setting thresholds for adaptive monitoring. Non-linearity and ‘hot-moments’ may be associated with different atmospheric, management, or accidental drivers (Krause *et al.*, 2015). For example when exploring atmospheric drivers such as precipitation, the river level or discharge would be an appropriate trigger variable given the focus on storm event dynamics. However, accidental releases (e.g. sewer

discharge, river bank collapse) would require a different trigger variable. While the parameter of interest could be used (see Figure 3d), the short windows associated with accidental release (Carstea *et al.*, 2010) could lead to an event being missed if it occurred between the coarse monitoring time steps (Figure 3c). In this case a surrogate variable with lower maintenance requirements could be monitored at high frequency (e.g. specific conductance or turbidity) providing a trigger for the nutrient analyser. Knowledge of the system is also particularly important for an effective adaptive monitoring strategy as catchment area and land use are both important and will influence the lag time between trigger and response (see section 4).



**Figure 3:** Conceptual representation of adaptive monitoring principals based on Krause *et al* (2015). Vertical dashed lines represent sample points, TT1 is trigger threshold 1 (black line), TT2 is trigger threshold 2 (red line) and TTa is an additional trigger threshold (horizontal dashed line). a) Hydrological context (precipitation and river level) and TTa, b) 'traditional' high resolution monitoring of a variable (nutrient) of interest, c) adaptive monitoring approach with TT1 and TT2

418 highlighted, (d & e) events of interest or 'active periods' highlighting the transition between the  
419 three monitoring frequency states based on threshold exceedance under rapidly changing  
420 environmental conditions. Note for a change from baseline monitoring frequency to higher  
421 resolution monitoring states TT1 & TTa must be exceeded to avoid inappropriate triggering.

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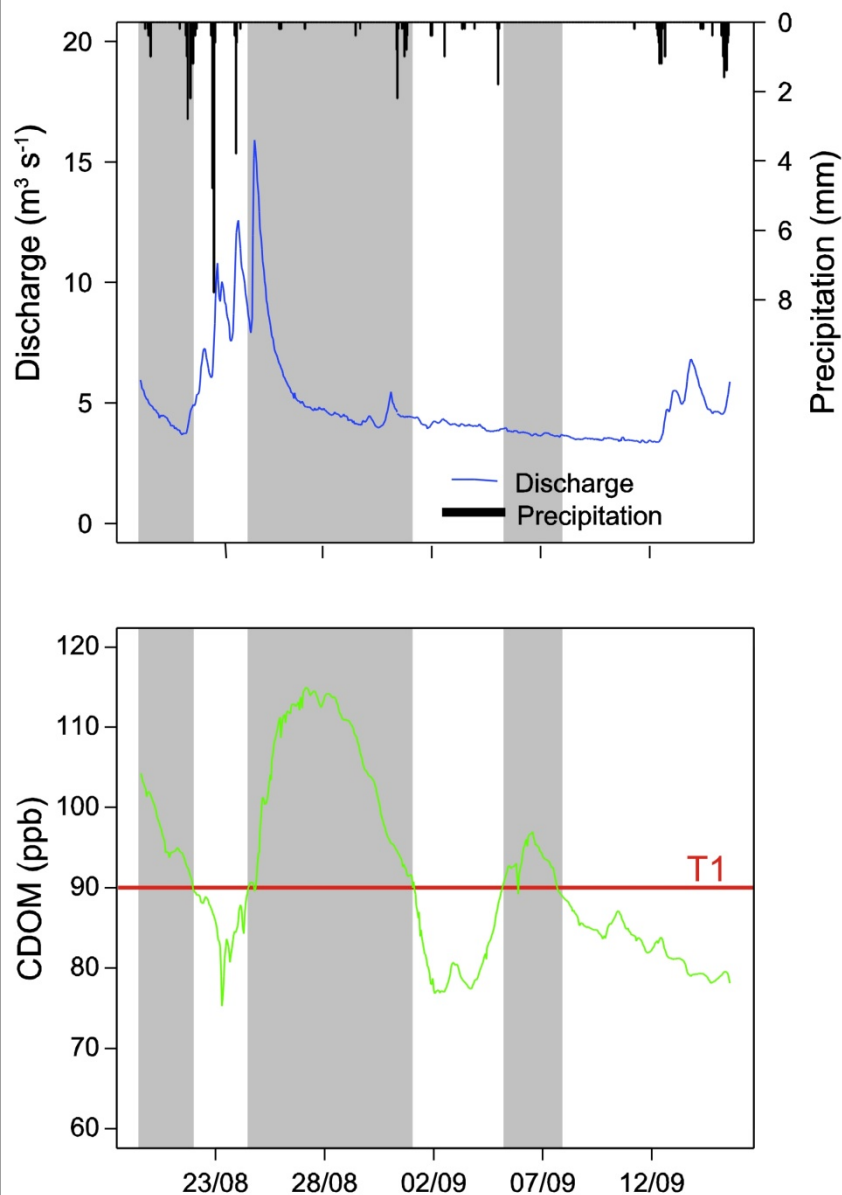
#### 4. Catchment variability in nutrient dynamics

In this section we present examples showing how novel monitoring strategies have delivered significant advances in process understanding and highlighted the variability in river nutrient dynamics in response to short-term drivers of change. In so doing, our aim is to demonstrate the extent and diversity of catchment differences in nutrient responses to which HRM could potentially be applied, thereby emphasising the need to develop site-specific sampling strategies (including thresholds and trigger variables) at frequencies appropriate to the parameters and system dynamics of interest. These thresholds should be reviewed regularly and updated where necessary to account for system behaviour changes caused by environmental, climate, or anthropogenic drivers. The examples illustrate the potential for adaptive real-time HRM strategies to capture nutrient dynamics during key hydrological events and hence improve our understanding of the catchment processes that underpin these patterns.

##### 4.1 River Wear, Durham, UK

The River Wear, Northern England (length = 106.9 km; catchment area: 1008km<sup>2</sup>) drains an area of the Eastern Pennines (see Neal *et al.* (2000) for a detailed description). During the autumn of 2015 CDOM fluorescence was monitored at the raw water intake of a water treatment works, close to a gauging station at Chester le Street, Northumbria (54°51'N, 1°33'W). The catchment is predominately grassland/moorland (~60 %) with minimal urban cover (<5 %) and a median altitude of 213 m. During the study period a mean lag time of ~18hrs between rainfall and peak flow was observed (Figure 4). A significant pulse of coloured dissolved organic matter (CDOM) was recorded after rainfall events between 23/09/15 and 24/09/15. However, peak CDOM lagged peak discharge by 56 hr, suggesting the primary source of CDOM at this site is the organic rich soils and peats in the upper catchment (Neal *et al.*, 2000). Thus, the delayed peak is likely due to a combination of: (i) wetting up time (i.e. time taken for shallow flow paths to activate); and, (ii) transit time to the monitoring site ~60km from the headwater CDOM sources (Hangen *et al.*, 2001; Inamdar and Mitchell, 2006). In this case, due to the apparent disconnection between river flow and CDOM concentration, precipitation and discharge would not be suitable triggers for changing monitoring frequency (adaptive HRM). However, due to the lengthy rising and falling limbs of the CDOM chemograph, the variable of interest would be an effective trigger. Here, given the lagged and relatively gradual response, it would be possible to represent the CDOM chemograph variability with relatively low frequency sampling (i.e. hourly).

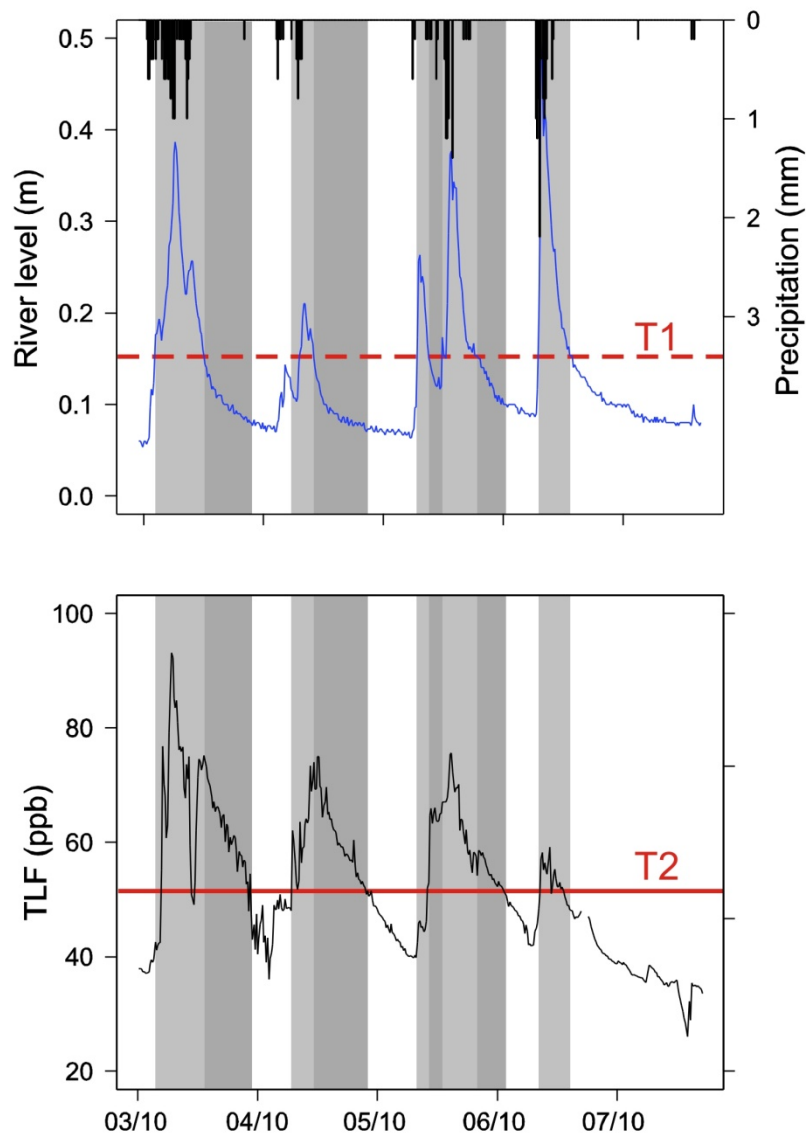




**Figure 4:** High resolution (15 min), *in-situ*, fluorescence and hydrological monitoring records from the River Wear. CDOM (coloured organic matter) was measured using a submersible CDOM fluorometer (Cyclops 7, Turner Inc.; Ex. 365nm, Em.460nm). A strong relationship between Total Organic Carbon (TOC) and CDOM was recorded ( $R^2 = 0.97$ ,  $n=11$ ). An example of adaptive monitoring is shown by grey bars that denote a switch from low to high sampling frequency triggered by CDOM exceeding a defined threshold (T1).

#### 4.2 Bourn Brook, Birmingham, UK

The Bourn Brook, a headwater tributary of the River Rea, is a small lowland stream (length = 7.4 km) in central England. During the autumn of 2014 a monitoring station recording river level and tryptophan-like fluorescence (TLF) was established close to the University of Birmingham campus (52°27'N, 1°54'W). The upstream catchment of 27.9 km<sup>2</sup> is mainly urban with a median altitude of 169 m asl. The site displays a distinct urban hydrology (Gurnell *et al.*, 2007) with a flashy flow regime and <2h lag time to peak flow (Figure 5). The organic matter dynamics for this site display a classic first flush effect (Lee and Bang, 2000), with TLF peaking either on the rising limb or at peak flow (Figure 5b). This suggests DOM sources are situated close to or in the channel, and probably include dry deposition on impervious surfaces and the breakup of biofilms in the channel, storm drains and combined sewer overflows (Carstea *et al.*, 2009; Khamis *et al.*, 2015). Thus, for this system, suitable triggers for adaptive monitoring would be a combination of river level/discharge and TLF (cf. Fig. 3). However, it is important to consider the purpose of the investigation as the adaptive monitoring approach outlined above would miss point source pollution event dynamics because the Boolean argument (level *AND* TLF) would not be satisfied.



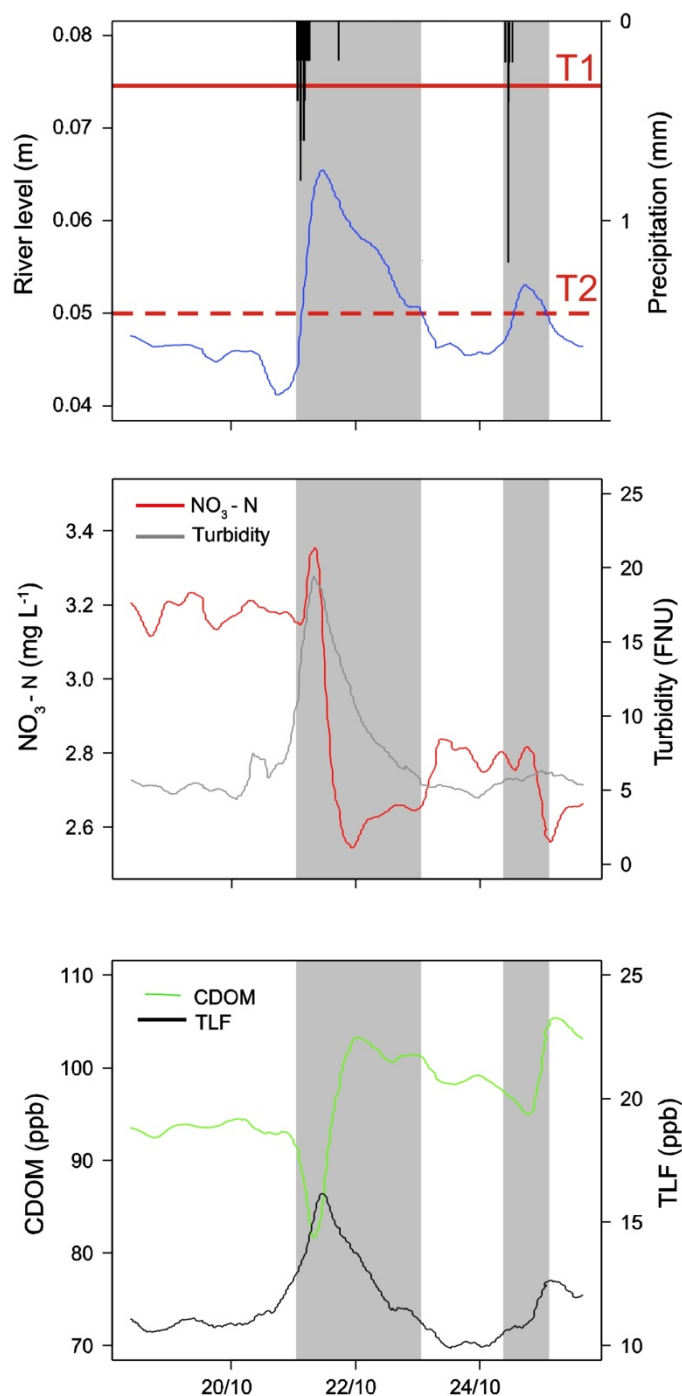
**Figure 5:** High resolution (15 min), *in-situ*, fluorescence and hydrological monitoring records from the Bourn Brook. TLF (tryptophan-like fluorescence) was measured using a Cyclops 7 fluorometer (Ex. 285 nm, Em. 350 nm). A strong relationship between Biochemical Oxygen Demand (BOD) and TLF was observed ( $R^2=0.92$ ,  $n=21$ ). An example of adaptive monitoring is shown by grey bars that denote a switch in sampling frequencies controlled by Boolean logic as follows: level > T1 = high frequency monitoring (light grey bars); level < T1 AND TLF > T2 = medium frequency monitoring (dark grey bars); level < T1 AND TLF < T2 = low frequency monitoring.

#### 4.3 Mill Brook, Staffordshire, UK

The Mill Brook, central England, drains 3.5 km<sup>2</sup> of arable farmland and a mixture of mature and new-growth deciduous woodland. The stream flows through the Birmingham Institute for Forest Research (BIFoR) field site where a permanent monitoring station was established in January 2015. A suite of water quality variables are currently analysed *in-situ* at 10-minute resolution, including spectrophotometer measurements of NO<sub>3</sub>-N and fluorometer measurements of CDOM and TLF. Data recorded to date suggest the system responds rapidly to precipitation events and that nutrient dynamics are driven strongly by changes in discharge (Figure 6). Both NO<sub>3</sub>-N and CDOM decrease markedly in response to increased discharge, whilst TLF increases with discharge. However, HRM allows shorter-term nutrient dynamics to be identified, most notably an initial increase in NO<sub>3</sub>-N concentration associated with the onset of precipitation events. This may be driven by the mobilisation and flushing of nitrate-rich waters in agricultural tile drains, which are common in agricultural watersheds (Wagner *et al.*, 2008). At Mill Brook, an increase in monitoring frequency (e.g. from hourly to 10 minute) triggered either by precipitation or increasing stream stage is necessary to capture the role of specific hydrological events for nutrient export (particularly NO<sub>3</sub>) from the catchment.

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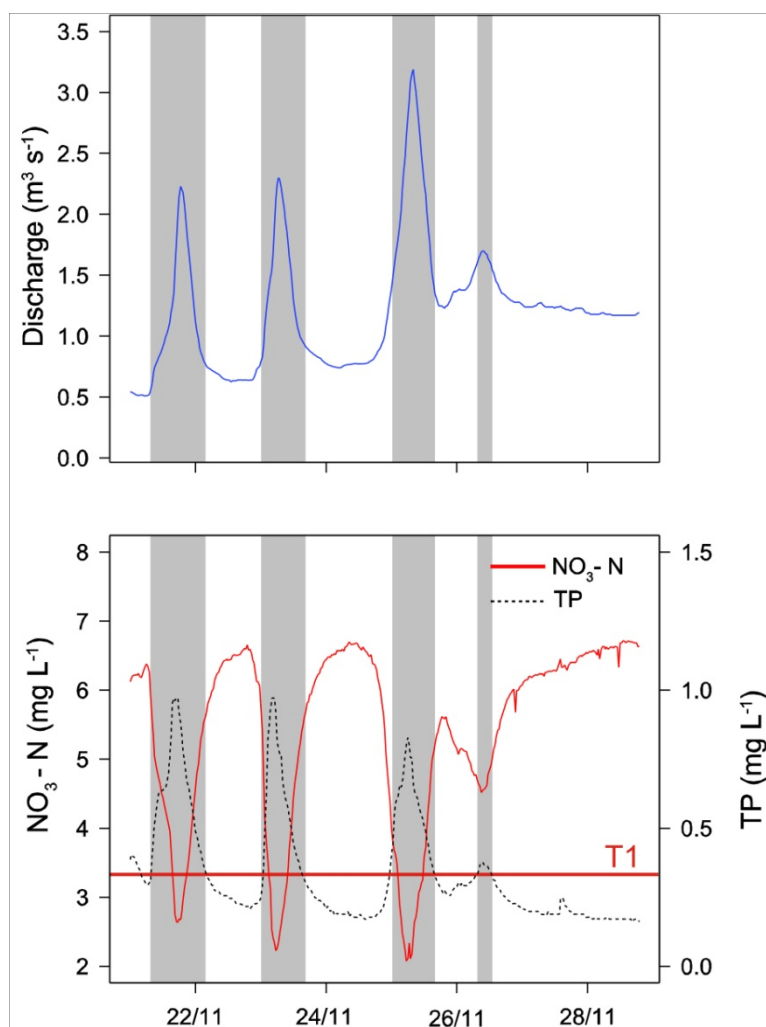
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**Figure 6:** High-resolution 10 minute monitoring data from the Mill Brook at the Birmingham Institute for Forest Research (BIFoR) field site in Staffordshire, UK.  $\text{NO}_3\text{-N}$  is determined using an optical Trios Opus UV spectrophotometer. CDOM (chromophoric dissolved organic matter) and TLF (tryptophan-like fluorescence) are measured using Turner Inc. Cyclops-7 fluorometers (Ex. 325nm, Em.460nm and Ex. 285 nm, Em. 350 nm, respectively). An example of adaptive monitoring is shown by grey bars that denote a switch from low to high sampling frequency initiated when precipitation > T1 and ended when level < T2.

#### 4.4 River Wylye, Wiltshire, UK

The River Wylye, a chalk stream in Southern England, is a headwater tributary of the Hampshire Avon. A monitoring station was installed at Brixton Deverill in 2011 as part of the Demonstration Test Catchment Programme, which aimed to use HRM of hydrochemistry to test the efficacy of on-farm pollution mitigation strategies (McGonigle *et al.* 2014). The station was located close to an existing gauging station (EA gauge 43806) which provided 15 minute resolution discharge measurements. At this point, the river drains 50 km<sup>2</sup> of agricultural land dominated by intensive mixed arable farming. The catchment hydrology has a significant groundwater contribution, resulting in slow baseflow variations in response to rainfall. Superimposed on this signal are flashy hydrological responses arising from direct input of precipitation and local surface runoff. The storm events illustrated in Figure 7 show a rapid response in both NO<sub>3</sub>-N and TP to increasing discharge. NO<sub>3</sub>-N shows a dilution response due to surface-water input, as the main source of NO<sub>3</sub>-N in the river is groundwater. Conversely, storm events resulted in pulses of TP at the monitoring station. HRM allowed the change in the lag between peak discharge and peak TP to be monitored across storms. Of the four storms shown here, the first storm resulted in an immediate TP response, most likely due to the remobilisation of bed sediments deposited at lower flow (Ballantine *et al.* 2009; Dorioz *et al.* 1998). Subsequent storms show an increasing lag between the discharge peak and the TP peak indicating a longer transit time for the pulse of TP to reach the monitoring station (Lloyd *et al.*, 2016; Bowes *et al.* 2005). These data highlight the importance of HRM to understand the transport mechanisms responsible for nutrient delivery to the stream during storm events. This also supports the argument for adaptive sampling strategies so that intense monitoring is undertaken only when it provides the maximum information about system processes driven predominantly by short-term event-based dynamics.



**Figure 7:** High-resolution 30-minute monitoring data from the River Wylfe at Brixton Deverill, collected as part of the Demonstration Test Catchment Programme. Discharge data were provided by the Environment Agency (England) and other data were provided by the Hants Avon DTC consortium (2016).  $\text{NO}_3\text{-N}$  was determined using an optical UV Hach Lange Nitratax sensor and TP was measured using a Hach Lange Phosphax Sigma bankside analyser which uses colorimetry following sample digestion. An example of adaptive monitoring is shown by grey bars that denote a switch from low to high sampling frequency triggered by TP exceeding a defined threshold (T1).

## 5. Conclusions and future directions

Recent technological advances in a number of areas have significantly enhanced our ability to monitor the major nutrients and DOM in rivers in real-time. This has the potential to revolutionise our capacity to understand and quantify the complex spatial patterns and temporal dynamics of biogeochemical cycling in systems sensitive to environmental change. Such developments facilitate insights into the wider significance of nutrient cycling and transformation processes, in particular at

biogeochemical hotspots and during hot moments of biogeochemical activity. Extending our perspective to fully capture the dynamic behaviour of catchment nutrient fluxes and transformations requires wider, integrated, application of the sensing technologies outlined above. For example, further development of semiautonomous sensing networks providing data at sufficient spatial and temporal resolution to monitor and model catchment biogeochemistry and hydrology and their links with ecosystem functions represent important advances (Crawford *et al.*, 2015). In particular, improvements in telemetry and developments in adaptive sampling have the potential to provide a step change in our understanding of dynamic systems but the potential of the currently available technologies has yet to be fully utilised. The examples discussed in this review illustrate some of the advances in process understanding that are possible by integrating new technologies for determining nutrient concentrations in aquatic systems with high resolution monitoring systems. The ability to specify particular triggers for sample collection, or for changing the temporal resolution of data collected, has the potential to make autonomous *in-situ* sampling more efficient and enhance our ability to capture system behaviour: quantifying the importance of fluxes associated with extreme hydrological events and yielding improved estimates and understanding of nutrient cycling through river catchments from their headwaters to the freshwater - marine transitional zone and beyond.

Improving our understanding of complex nutrient cycles and their interactions across ecosystem boundaries represents significant interdisciplinary challenges. For example, whilst HRM can be invaluable in improving our estimates of nutrient fluxes, there remains a need for greater cross-disciplinarity across the different facets of aquatic monitoring programmes. Historically there has been a distinct mismatch between standard ecological sampling protocols and nutrient / chemical monitoring schemes. As a result, potentially important feedbacks between ecology and biogeochemical cycling may be missed. However, promising advances in real-time, automated species recognition tools (e.g. Aide *et al.*, 2013) could herald a new era of ecosystem monitoring in which our ability to monitor physiology and movement could be complemented by real-time nutrient monitoring (Kuklina *et al.*, 2013).

To a considerable extent, our understanding of these processes to-date has been constrained by the distribution and density of monitoring locations, which in many cases reflect high instrumentation costs and limited funding availability. Recent and future developments of low cost and open-source sensors for water quality monitoring have enormous potential here; particularly the combination of micro-controllers and 3-D printers. For example, Leeuw *et al.*, (2013) outline the development of an *in-situ* fluorescence sensor for chlorophyll *a*, with a unit cost (in 2013) of US\$ 150, while Wittbrodt *et al.*, (2015) provide details of a low cost nitrate sensor using the Nitrate Reductase Nitrate – Nitrogen Analysis Method. Given the significantly reduced cost of these new open source products, greater densities of *in-situ* riverine nutrient monitoring networks should be feasible, matching advances in urban air quality monitoring (Mead *et al.*, 2013).

Further exciting advances can be expected by fully utilising the potential to link outputs from autonomous sensor networks to Earth Observation (EO) platforms. Recent and ongoing developments in EO provide opportunity for enhanced water quality monitoring and assessment in freshwaters, transitional zones, through to marine environments (Tyler *et al.* 2016). While EO data are now used routinely for marine observation, river applications are constrained by spatial resolution, and costs for data acquisition, particularly for new platforms (e.g. Dugdale *et al.*, 2015).



However, the spatial resolution of new sensors and platforms, such as PACE / Worldview-3, at >1m, opens opportunities to capture spatial trends in nutrient dynamics (e.g. CDOM) or proxy indicators, such as turbidity as a proxy for TP (Viviano *et al.*, 2014). Inevitably, however, these applications will rely upon extensive field verification with appropriate quality assurance and control. This may be facilitated by automated sensor recalibration, but given the spatial and temporal variability in nutrient transfer, catchment-specific calibrations of individual sensors may be necessary (cf. Khamis *et al.* 2015) and time-invariance in sensor calibration parameters should not be assumed.

As data of increasing spatial and temporal resolution become available, the maintenance of long-running data-sets is becoming increasingly important (Holmes, 2006; Burt *et al.*, 2010) to capture the extent of 'natural' environmental variability (Crawford *et al.* 2014) and to develop hypothesis-driven science and monitoring to advance our understanding of system behaviour. There is now scope for the wider application of recent technological advances to provide greater insight into the wider biogeochemical functioning of river catchments, particularly with reductions in sensor costs, and increasing availability of EO data. If practical problems, for example with respect to power supply and biofouling, can be resolved, these developments offer a potential paradigm-shift in our understanding of environmental complexity (cf. Krause *et al.* 2015), our ability to characterise the fluxes of key nutrients from catchments-to-coast, and our understanding of the spatial variability in freshwater biogeochemistry and hydrology.

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